

[19] State Intellectual Property Office of P. R. China

[51] Int. Cl⁶

C08F110/02

C08F 4/60

C08F 2/34

[12] Invention Patent Application Public Description

[12] Application No.: 97106144.0

[43] Date of Publication: April 21, 1999

[11] Publication No.: CN 1214344A

[22] Application Date: October 13, 1997

[21] Application No.: 97106144.0

[71] Applicant: Qilu Petrochemical Corp. of SINOPEC
Address: P.O. Box 124, Zibo City, Shangdong Province, China
255408

[72] Inventor(s): Jianwen Da, Liuzhong Li, Tingshan Zhang,
Hong Ren, Puyun Miao, Shengchun Liu, and Jie Yan

[74] Patent Agency: Patent Firm of Qilu
Petrochemical Corp.
Patent Agent: Hongyan Du

Claims : 2 pages
Description: 8 pages
Attached Drawings: 0 page

[54] Title of Invention: a Ziegler-type catalyst and its
preparation technique, which is applicable in the gas-phase
method ethylene polymerization process

[57] Abstract

This invention relates to a Ziegler-type catalyst and its
preparation techniques, which are applicable in gas-phase
method ethylene polymerization processes. The catalyst has
such characteristics as high activation, strong copolymerization
properties, and wide distribution of the product's molecular
weight. It may be used in ethylene gas-phase homo-
polymerization. It may be also used with α -alkene
copolymerization to produce low-pressure high-density
polymerizing ethylene or low-and-medium density
polymerizing ethylene.

ISSN 1008-4274

Published by Patent Records Press

Claims

1. A Ziegler-type catalyst applicable in the gas-phase method ethylene polymerization process includes the following processes: impregnate the difficult-to-melt inorganic oxide support, the surface of which contains alkyl, into an inorganic chromium compound water solution, after being dried, roasted, and reduced, to produce the catalyst. The feature of the process is to adopt the organic aluminum compound as the reducer.
2. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said reducer is the organic aluminum compound with the following formula:



Whereas, R or R' is the alkyl of 1 ~ 20 carbon atoms. These two may be the same or different; x or y is the integral number ranging from 1 to 3. These two may be same or different.

3. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said organic aluminum reducer is the organic aluminum compound such as AlR_3 and $ROIR'_2$.
4. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said organic aluminum reducer may also be the partial water solution of the alkyl aluminum compound such as MAO, EAO, BAO, i-BAO, and EBAO.
5. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said inorganic oxide support are SiO_2 , Al_2O_3 , $SiO_2-Al_2O_3$, and TiO_2 .
6. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that, among the said inorganic oxide support, the oxidized silica support is better.
7. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the said inorganic chromium compounds include chromium oxide, inorganic salt, acetate, oxalate, chromium nitrate, bichromate, and chromate such as CrO_3 , $(NH_4)_2Cr_2O_7$, $Cr(Ac)_3$, $Cr(C_2O_4)_3$, $CrCl_3$, and $Cr(NO_3)_3$.
8. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the content of the said inorganic chromium support, measured at the support weight, is 0.01 ~ 5.0wt%.
9. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that the content of the said inorganic chromium support, measured at the support weight, is 0.05 ~ 1.5wt% for the better ones.
10. The feature of the said catalyst in the Item 1 of the Claims lies in the fact that it is roasted at a temperature of 300 ~ 800 °C.

11. The feature of the preparation technique of a Ziegler-type catalyst applicable in the gas-phase method ethylene polymerization process lies in the fact that this preparation technique includes the following processes:

(A) Have the inorganic chromium compound dissolved in distilled water or prepare a water solution from deionized water;

(B) Impregnate the inorganic oxide support such as the SiO_2 , Al_2O_3 , the surface of which contains the alkyl, into the solution prepared from the Step (A);

(C) Dry the solution in the Step (B) in the air to a free flow condition;

(D) Activate, in the oxygen-containing ambient, the particle in the Step (C) under the fluidization conditions;

(E) Put the midbody of the catalyst, which is activated in the Step (D), into the inert organic solvent medium; reduce it with an organic aluminum reducer in the inert ambient; dry it to a good flow condition, producing the catalyst;

12. The feature of the said preparation technique of the catalyst in the Item 11 of the Claims lies in the fact that, in activation, it takes 0.5 ~ 12 hours to activate at a temperature of 300 ~ 800 °C.

13. The feature of the said preparation technique of the catalyst in the Item 11 of the Claims lies in the fact that, in reduction, it takes 0.1 ~ 4 hours to contact at a temperature of 10 ~ 80 °C.

Explanations

A Ziegler-type Catalyst and its Preparation Technique, Which is Applicable in the Gas-phase Method Ethylene Polymerization Process

This invention relates to a Ziegler-type catalyst and its preparation technique, which is applicable in the gas-phase method ethylene polymerization process, and particularly the Ziegler-type chromium-containing solid catalyst and its preparation technique applicable in the gas-phase method ethylene polymerization process.

The Ziegler-type chromium-containing solid catalyst is one of the earlier types of successfully developed catalysts in the field of the ethylene polymerization. This type of the catalyst generally includes two categories: the inorganic chromium (oxidized chromium) and organic chromium. U.S. patent No. 2,825,721 published a catalyst of the Ziegler-type oxidized chromium. The water solution of such chromium compounds as chromium trioxide is used to impregnate the support. The catalyst, after being dried and roasted, is produced and is applicable in synthetic products with a narrower distribution of molecular weight. In comparison, oxidized chromium catalyst overcomes the weakness of organic chromium catalysts due to the complicated synthetic process of organic chromium with activation components. The advantage of its low cost is evident in producing inorganic-chromium type catalysts. However, the application scope of the inorganic chromium-type catalyst is limited due to the following shortcomings: the oxidized chromium-type catalyst itself requires a long time for polymerization to occur; the hydrogen peroxide is insensitive; the property of the copolymerization is poor; the melt index of the synthetic products is low; and the distribution of the molecular weight is narrow. Therefore, there are many improved types of inorganic chromium-type catalysts. U.S. Patent number 4,735,931 uses CO as a reducer to increase the melt index of the products, but it is still difficult to overcome the following problems: the length of time for polymerization for traditional oxidized chromium catalysts, their poor copolymerization characteristics, and narrow distribution of molecular weight. In U.S. patent No. 4,877,763 and U.S. patent No. 5,284,926, prior to the polymerization reaction, the micro organic aluminum and organic boron compounds are separately added into the reactor to increase activation of polymerization and the melt index of the products, and to improve the distribution of molecular weight. However, it complicates the process of the polymerization process to directly add the reducer of the organic metal compound into the reactor. Moreover, the time and amount of the reducer to be added must be strictly controlled and measured. In addition, the said improved catalyst is mainly for the ethylene polymerization process in the slurry process. It does not deal with the oxidized chromium-type catalyst applicable in the gas-phase method ethylene polymerization process.

The objective of this invention is to overcome the shortcomings of the said improved oxidized chromium-type catalysts and to provide a Ziegler-type solid catalyst, applicable in the gas-phase method ethylene polymerization process, of the high activation and the strong copolymerization properties.

Another objective of this invention is to provide the preparation technique of the Ziegler-type chromium catalyst applicable in the gas-phase method ethylene polymerization process.

To reach the above objectives, the outline of the technical scheme we adopt is as follows:

- (1) Have the inorganic chromium compound dissolved in distilled water or prepare a water solution of 0.01 ~ 5.0 mol/l from deionized water;
- (2) Put an inorganic oxide support such as SiO_2 and Al_2O_3 , the surface of which contains alkyl, into the solution with inorganic chromium and impregnate it for 5 ~ 10 hours at a temperature of 10 ~ 80°C. Measured by the weight of the support, the content of the chromium is 0.01 ~ 5.0wt% or, most preferably 0.05 ~ 1.5wt%.
- (3) Dry the solution in the Step (2) in the air for 5 ~ 48 hours or, most preferably, for 12 ~ 24 hours at an air temperature of 80 ~ 120°C to a free flow condition.
- (4) Activate, in an oxygen-containing ambient of 150 ~ 950°C, place the particle in the Step (3) under fluidization for 0.5 ~ 12 hours or, most preferably, for 1 ~ 8 hours at a temperature of 300 ~ 800°C.
- (5) Put the midbody of the catalyst, which is activated in the Step (4), into the inert organic solvent medium; reduce it with the organic reducer in an inert ambient for 0.1 ~ 4 hours at a temperature of 10 ~ 80°C; then dry it to a good flow condition in the inert air flow, producing the catalyst. The inert gases are the pure and high nitrogen, helium, or argon.

The chromium compound referred in this invention include the majority of inorganic chromium compounds such as CrO_3 , including chromium oxide, inorganic salt, acetate, oxalate, chromium nitrate, bichromate, and chromate.

The catalyst support of this invention adopts the difficult-to-melt inorganic oxide support, the surface of which contains alkyl, such as SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, and TiO_2 . The better ones are those oxidized silica supports that have a ratio surface of 150 ~ 350 cm^3/g , an aperture of 10 ~ 50nm, and a particle size of 10 ~ 200 μm .

The organic reducer adopted in this invention is a metal organic compound, primarily the organic aluminum compound such as the triisobutyl aluminum, trimethyl aluminum, triethyl aluminum, ethoxyl diethyl aluminum, methyl aluminum oxysilane, ethyl aluminum oxysilane, butyl aluminum oxysilane, and other similar compounds. Its formula can be expressed as:



Whereas, R or R' is the alkyl of 1 ~ 20 carbon atoms. These two may be the same or different. The x or y is an integer ranging from 1 to 3. These two may be the same or different. The said organic metal compound may be used independently, or two or more may also be used together. The amount of the organic aluminum compound is related to the amount of the chromium-containing compound which is carried by the support. The Al/Cr ratio (the molar ratio) denotes its relative amount. The Al/Cr ratio is normally within the range of 0 ~ 50, while the better amount is within the range of 0.5 ~ 20. The objective of adding the organic aluminum compound is to reduce the high valence aluminum (+6), after being roasted, into the polymerization active

site with a series of different low valences, which is helpful to produce polyethylene resin of high density or medium density, with wider distribution of molecular weight.

The inert organic solvents adopted in this invention include saturated paraffins or pentane, isopentene, hexane, heptane, pure kerosene, and other similar paraffins; saturated cycloparaffins such as the cyclohexenyl, cyclopentane, dimethyl cyclopentane, methyl cyclohexenyl, and other similar cycloparaffins; arenes such as the benzene, methylbenzene, xylene, and other similar arenes; preferable solvents are isopentene, pentane, hexane, heptane, and cyclohexenyl.

The catalyst in this invention can be used for gas-phase polymerization reactions. The gas-phase polymerization reaction device can be either a gas-phase stir bed cauldron or a gas-phase fluidization bed reactor. Prior to polymerization, the catalyst can directly undertake the polymerization reaction without going through prepolymerization. The said homo-polymerization refers to polymerization of ethylene without having a copolymerization monomer. The said copolymerization refers to the copolymerization reaction of ethylene and α -alkene, which is aimed to reduce the density of polyethylene resin products. The adopted α -alkene refers to α -alkene that contains 3 ~ 20 carbon atoms, while the better ones are those α -alkenes that contain 3 ~ 8 carbon atoms, including propylene, 1-butene, 1-hexene, 4-methyl-pentene-1, and 1-octene. The temperature range of the polymerization is 20 ~ 150 °C, while the better one is 50 ~ 120 °C. The pressure of the polymerization reaction is 0.05 ~ 5MPa, while the better one is 0.1 ~ 3MPa.

In evaluating the catalyst, this invention uses a gas-phase stir bed cauldron and adopts the technique of gas-phase polymerization. The reactor is a high pressure cauldron made of stainless steel and with a volume of 1 liter. It has a cauldron cover that can be fixed with bolts and screws. The reactor is equipped with blenders, a flow conductor, a temperature control jacket, a pressure monitoring device, and tubes that lead the reaction gases, hydrogen, nitrogen, copolymerization monomer into the reactor.

During the polymerization reaction process, computers are used to control and measure temperature and pressure. The ethylene monomer is added through the mass flow meter. The radiotube is used to control the addition of the copolymerization monomer and hydrogen. The following steps are taken: have the cauldron under vacuum treatment for about 2 hours, during which pure and high nitrogen is impregnated multiple times and replaced 6 ~ 10 times; increase, through the thermostatic water baths, the temperature of the cauldron up to slightly below the reaction temperature; add the catalyst under the protection of the pure and high nitrogen; extract the nitrogen after dispersing it; add the ethylene to the pressure needed for the reaction; begin to keep track of time from the beginning of the reaction. The following formula is used to calculate the polymerization yield:

$$W_{\text{poly}} = (Q \cdot 60) / (t_{\text{poly}} \cdot W_{\text{cat}}), \quad \text{g} \cdot \text{PE} / \text{g} \cdot \text{Cat} \cdot \text{h}$$

Whereas, Q is the yield (g) of the polymer within the time t (minutes) of the polymerization reaction, W_{cat} is the amount of catalyst. Once the polymerization reaction is completed, the reaction is terminated by discharging reaction gases.

The extraordinary features of this invention are as follows:

- (1) This catalyst uses the inorganic chromium compound as raw a material, which is cheap to buy and easy to obtain, so the cost is lower.
- (2) The organic aluminum compound is used as the reducer, to greatly reduce the time of the reduction; the need for high temperatures is reduced, which saves time and energy.
- (3) In the evaluation, this catalyst adopts the gas-phase method, which is applicable in the gas-phase fluidization bed process, with the advantages of the less investment, lower energy consumption, and lack of waste.

In order to better elaborate this invention, we present the following examples; however, this invention is not limited to the following examples.

For the polymer produced in the examples, melt flow velocity is determined in accordance with ASTM D 1238-65T, and the density is determined in accordance with ASTM D 1505-68.

Example 1

Put 0.5g CrO_3 into a millimeter small mouth flask, adding distilled water or deionized water to prepare a 0.05mol/l water solution before use. Weigh and put 10g Davision 955 silica gels into the 100ml flask; then, using a piette, take and move 9.62ml of the said 0.05mol/l water solution, and add it into the flask; after agitating it finely, dry it at an air temperature of 80 ~ 120°C for 12 hours to a good flow condition; put into a $\Phi 30 \times 500\text{mm}$ quartz fluidization bed, the bottom of which is welded with a micropore sinter quartz sparge plate; introduce dry air, which is dewatered through 13X molecular sieves; make it dewater further in a fluidized state. The temperature increase process takes 2 hours at 200°C, and then 4 hours at 600°C; at last, switch into the pure and high nitrogen, which is dewatered through the 13X molecular sieves, and keep it for 1 hour at the 600°C; under the fluidization and in the nitrogen, cool it down to the room temperature and take it out before use. Under the protection of the said pure and high nitrogen, add 1g of the said support CrO_3 silica gels; then add 0.35ml 25% (m/m) hexane solution of the ethoxyl diethyl aluminum; treat it for 1 hour under the condition of the tight-controlled agitation; then use the dry pure and high nitrogen to blow away the solvent, producing the powder catalyst with 0.25wt% of the amount of chromium contained with an Al/Cr ratio of 3.

Examples 2 ~ 4

The preparation technique of the catalyst in the examples 2 ~ 4 is similar to that in the example 1. The difference is that examples 2 ~ 4 respectively use triethyl aluminum, tri-butyl aluminum, and methyl aluminum oxysilane to get the powder catalyst with 0.25wt% of the amount of the chromium contained with an Al/Cr ratio of 3.

Subject Example 1

Put 0.5g CrO_3 into a 100ml small mouth flask, add distilled water or deionized water to prepare a 0.05mol/l water solution before use. Weigh and put 10g Davision 955 silica gels into a 100ml flask; then, using a piette, take and move 9.62ml of the said 0.05mol/l water solution and add it into the flask; after agitating it finely, dry it at an air temperature of 80 ~ 120°C for 12 hours to a better flow condition; put into a $\Phi 30 \times 500\text{mm}$ quartz fluidization bed, the bottom of which is welded with a micropore sinter quartz sparge plate; introduce dry air, which is dewatered through 13X molecular sieves; make it dewater further in a fluidized state. The temperature increase process takes 2 hours at 200°C and then 4 hours at 600°C; finally, switch it into the pure and high nitrogen, which is dewatered through 13X molecular sieves, and keep it for 1 hour at the 600°C; under the fluidization and in the nitrogen, cool it down to room temperature and take it out, producing a traditional oxidized chromium catalyst.

Subject Example 2

Put 0.5g CrO_3 into the 100ml small mouth flask, adding distilled water or deionized water to prepare a 0.05mol/l water solution before use. Weigh and put 10g Davision 955 silica gels into the 100ml flask; then, using a piette, take and move 9.62ml of the said 0.05mol/l water solution and add it into the flask; after agitating it finely, dry it at a air temperature of 80 ~ 120°C for 12 hours to a better flow condition; put it into a $\Phi 30 \times 500\text{mm}$ quartz fluidization bed, the bottom of which is welded with a micropore sinter quartz sparge plate; introduce the dry air, which is dewatered through 13X molecular sieves; make it dewater further in a fluidized state. The temperature increase process takes 2 hours at 200°C and then 4 hours at 600°C; and then, switch it into the pure and high nitrogen, which is dewatered through 13X molecular sieves, and lower the temperature down to 350°C; then switch it into CO gas at 350°C and reduce it for 2 hours; finally, switch it into the said pure and high nitrogen and maintain for 1 hour; after that, under the fluidization and in the nitrogen, cool it down to room temperature and take it out before use, thus producing the CO reduction chromium catalyst.

The catalyst made from the examples 1 ~ 4 and from the subject examples 1 and 2 is separately used for polymerization reactions with the results presented in the Table 1.

Examples 5 ~ 7

The preparation technique of the catalyst in examples 5 ~ 7 is similar to that in the example 1. The difference is that in examples 5 ~ 7, the Al/Cr ratio (molar /molar) is respectively 1, 6, and 10 in producing the powder catalyst.

Examples 8 ~ 10

The preparation technique of the catalyst in examples 8 ~ 10 is similar to that in example 1. The difference is that in the examples 8 ~ 10, the amount of the chromium Cr wt% is respectively 0.1, 0.15, and 0.5, in producing the powder catalyst.

Examples 11 ~ 13

The preparation technique of the catalyst in examples 11 ~ 13 is similar to that in example 1. The difference is that in examples 11 ~ 13, the activating temperature is respectively 400°C, 500°C, and 800°C, in producing the powder catalyst.

The catalyst made from the examples 5 ~ 13 is separately used for polymerization reaction with the results presented in the Table 2.

Examples 14 ~ 16

Use the catalyst produced in example 1 and follow the evaluation methods provided in this invention, with the H_2/C_2H_4 ratio as 0.02, 0.06, and 0.10, respectively; weigh and test the powder of the polyethylene products with the results presented in the Table 3.

Examples 17 ~ 19

Use the catalyst produced in the example 1 and follow the evaluation methods provided in this invention, with the C_3H_6/C_2H_4 ratio as 0.006, 0.012, and 0.020, respectively; weigh and test the powder of the polyethylene products with the results presented in the Table 4.

Examples 20 ~ 22

Use the catalyst produced in the example 1 and follow the evaluation methods provided in this invention, with -butene as the copolymerization monomer and the C_4H_8/C_2H_4 ratio as 0.006, 0.012, and 0.020, respectively; weigh and test the powder of the resulting polyethylene products with the results presented in the Table 5.

Table 1

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	Catalyst		Polymer Yield gPE/gCat.h	$I_{21.5}$ g/10min	Density g/cm ³
	Cr, wt%	Al/Cr			
Example 1	0.25	3	236	25.31	0.9582
Example 2	0.25	3	285	3.59	0.9587
Example 3	0.25	3	379	3.56	0.9598
Example 4	0.25	3	481	5.25	0.9606
Subject Example 1	0.25	3	186	1.54	0.9631
Subject Example 2	0.25	0	202	6.46	0.9648

Table 2

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	Catalyst				Polymer Yield	I _{21.5}	Density
	Cr, wt%	Reducer	Al/Cr	Activating Temperature °C	gPE/gCat.h	g/10min	g/cm ³
Example 5	0.25	EtOAlET ₂	1	600	221	5.32	0.9612
Example 6	0.25	EtOAlET ₂	6	600	263	23.86	0.9597
Example 7	0.25	EtOAlET ₂	10	600	235	22.76	0.9586
Example 8	0.10	EtOAlET ₂	3	600	68	3.91	0.9588
Example 9	0.15	EtOAlET ₂	3	600	153	8.27	0.9593
Example 10	0.50	EtOAlET ₂	3	600	287	32.93	0.9635
Example 11	0.25	EtOAlET ₂	3	400	121	11.82	0.9596
Example 12	0.25	EtOAlET ₂	3	500	198	17.08	0.9598
Example 13	0.25	EtOAlET ₂	3	800	336	58.18	0.9606

Table 3

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	H ₂ /C ₂ H ₄ ratio	Ethylene Partial Pressure MPa	Nitrogen Partial Pressure MPa	Polymer Yield gPE/gCat.h	I _{21.5} g/10min	Density g/cm ³
Example 14	0.02	1.078	0.022	228	35.63	0.9524
Example 15	0.06	1.034	0.066	216	78.21	0.9512
Example 16	0.10	1.990	0.110	234	99.39	0.9503

Table 4

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	C ₃ /C ₂ H ₄ Ratio	Ethylene Partial Pressure MPa	Propylene Partial Pressure MPa	Polymer Yield gPE/gCat.h	I _{21.5} g/10min	Density g/cm ³
Example 17	0.06	1.093	0.007	235	38.69	0.9482
Example 18	0.012	1.087	0.013	226	42.64	0.9435
Example 19	0.020	1.078	0.022	243	45.27	0.9386

Table 5

Polymerization conditions: the reaction temperature is 95°C; the reaction pressure is 1.100MPa; the reaction time is 60 minutes.

No.	C-4/C ₂ H ₄ Ratio	Ethylene Partial Pressure MPa	Polymerization Partial Pressure MPa	Polymer Yield gPE/gCat.h	I _{21.5} g/10min	Density g/cm ³
Example 20	0.006	1.093	0.007	226	41.32	0.9468
Example 21	0.012	1.087	0.013	265	46.61	0.9413
Example 22	0.020	1.078	0.022	249	49.26	0.9364